1917
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A Study of the Specific Heats of Fats and Oils

A STUDY OF THE SPECIFIC HEATS OF FATS AND OILS

BY

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THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMICAL ENGINEERING

COLLEGE OF LIBERAL ARTS AND SCIENCES

UNIVERSITY OF ILLINOIS

1917

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Table of Contents.

Page

I Introduction--------------------- 1

II General Discussion--------------- 3

III Review of Methods---------------- 6

IV Experimental--------------------- 9

V Conclusion-----------------------18

A STUDY OF THE SPECIFIC HEATS OF FATS AND OILS.

I INTRODUCTION

This investigation was undertaken in order to determine the specific heats of some samples of fats and oils received by the department of Applied Chemistry from Morris and Company.

The main value of such data was in connection with the conveyance of such substances by pumping in the liquid form. For this and other reasons stated later, it was decided to determine the specific heats only in the liquid form.

The first problem which presented itself was a selection of the method to be used and a modification of it to meet the conditions. The standardization of the apparatus was then undertaken after which the work of determining the actual specific heats was begun. In consideration of the fact that the oils had been received sometime previous to the time this work was taken up, it was deemed advisable to determine some of the constants in order to ascertain in what condition the samples were. The specific gravity,

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saponification value and iodine number were accordingly determined and compared with the values given by Lewkowitsch[1] for the commercial oils. The results, as given in later tables, compared very well with the values given by Lewkowitsch.

The investigation was later extended to cover some of the other common edible oils and drying oils. It was also decided to study how the specific heats vary with the temperature, particularly those of the fats which are solid at room temperature.

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[1] Lewkowitsch - Chemical Technology and Analysis of Fats, Oils and Waxes.

II GENERAL DISCUSSION

That the specific heat was a well-defined function of the atomic and molecular weights was first stated in 1818 by Du Long and Petit who said that the product of the atomic weight of an element into its specific heat in the solid condition, is a constant. In other words, the atomic heat capacities of all solid elements are approximately the same. In some cases, however, the heat capacities must be measured at much higher than room temperature, notably in the case of carbon, silicon, boron and a few others.

This principle also holds fairly well for gases, the constant in this case, however, being only about one-half as great as in the case of solids.

With liquids, on the other hand, this principle does not hold at all, and so in work with liquids we are unable to make use of the law of Du Long and Petit or its two corollaries, those of Woestyn and Neumann, the first of which states that the molecular heat of a compound may be obtained by taking the sum of the atomic heats of its constituents, and the second, that for compounds of the same general formula, which are similarly constituted, the product of the molecular weights into the specific heats is a constant which varies with the series of compounds. Several investigations have been made to determine the specific heats of various solutions and liquid substances. A large propor-

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[illegible]

tion of these have been with inorganic substances or solutions of inorganic acids, bases or salts. It is found that whereas the specific heats of inorganic substances are not greater than .2 or .3, those of organic substances are generally greater than .3.

Of the organic substances investigated, comparatively few have been of the nature of fats. The reason for this, as stated by Vandeveyer and Parson[1] is that it is impossible to eliminate rises in temperature due to the heat of fusion or to distinguish between specific heat and heat of fusion when in the solid state. Even in the liquid state, the specific heats are not found to be constant with varying temperatures. Thus for olive oil, the specific heat as studied by Magie[2], Weber[3] and others, was found to vary between .396 and .471.

The reasons for investigating these fats and oils only in the liquid phase were as follows:

(1) The almost impossibility, as noted above, of obtaining the true specific heat of a solid fat.

(2) The low melting points of the only two solid fats studied.

(3) The fact, as stated in the introduction, that the data as to specific heats in the liquid state is of more importance in the case under consideration.

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[1] Ann. Chim. Anal. 5, 321.

[2] Phys. Reo. 13, 91; 9, 65; 17, 105; 14, 193.

[3] Wied. Ann. 10, 314.

The method used was essentially a method of mixtures and one of the principal obstacles to accuracy was radiation loss. This was compensated for in those samples which were run at room temperature by having the range of heating extend from about one to two degrees below room temperature to about two or three degrees above. In the case of those fats which were solid at ordinary temperatures or those determinations at higher temperatures of the liquid oils a correction was necessary. In order to make this, the rate of cooling was determined using corn oil in the calorimeter. The corn oil was heated and readings of temperature and time taken at ten second intervals, from which a curve was plotted showing relation between rate of radiation and temperature. By taking readings of the rise of temperature at ten second intervals during a determination and adding to each reading the rate of radiation as determined from the curve a final reading for the highest temperature could be obtained which was corrected for radiation.

III REVIEW OF METHODS

In regard to apparatus, the various forms that have been used show wide variation. Vandeveyer[1] used the method of mixtures, the fat being held in a metal container to be sure of its complete immersion in water. The specific heat of the container was obtained separately. In their work with fused salts, Goodwin and Kalmus[2] used a very similar apparatus. The salts were heated in sealed platinum cylinders, dropped into a calorimeter containing water and a mechanical stirrer and the rise of temperature was noted.

Dickinson and Mueller[3] used an electric coil to supply heat to a constant stream of liquid passing through a spiral in an insulated vessel.

Richards and Rowe,[4] in their work, developed an adiabatic calorimeter for use in work with liquids. In this instrument the heat was supplied to a given amount of the liquid by neutralization of a known amount of a standard solution of sulphuric acid with a known solution of sodium hydroxide, the sodium hydroxide in a small bulb suspended within the liquid and the sulphuric acid being led in through a small tube from a burette. The adiabatic feature was obtained by the use of a solution of sodium hydroxide in the

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[1] Ann. Chem. Anal. 5, 321.

[2] Phys. Rev. 28, 1-25.

[3] Phys. Rev. 26, 519.

[4] Zeit. phys. Chem. 84, 585-610.

outer vessel of the calorimeter and adding sulphuric acid as before to keep the temperature within the calorimeter and the temperature of the bath as near together as possible in order to eliminate radiation corrections.

An improvement was made upon this by Daniels and Richards[1] in that heat was supplied to the water in the outer jacket by passing a current directly through it using two metal vessels as electrodes. By the use of a sensitive thermocouple and galvanometer, the two junctions of the thermocouple being one in the water of the outer jacket and one in the liquid of the inner cup, a very slight difference of temperature could be shown and more current was then passed through the water of the jacket to bring it up to the temperature of the liquid. By using a galvanometer with a mirror and reflecting a beam of light on a selenium cell, the apparatus could be made entirely automatic and adiabatic to a high degree.

Possibly the best and most convenient method for determining the specific heat of a liquid when quantities of one to two liters are available is to use the liquid as a bath for absorbing heat in a standard bomb carloimeter or the Parr adiabatic calorimeter. In this case a known quantity of a standard substance is burned in the calorimeter bomb and the rise in temperature of the liquid is noted.

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[1] J. Am. Chem. Soc. 38, 1473.

The methods given above are probably the best of a large number reviewed and demonstrate the various principles made use of. More descriptions of methods may be obtained from the work of Karavayev,[1] Heydweiler,[2] Magnus[3] and Frantz[4].

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[1] J. Soc. Chem. Ind. 33, 128.

[2] Ann. Physik. 46, 253.

[3] Ann. Physik. 31, 597.

[4] Physikal. Zeit. 14, 1176.

IV EXPERIMENTAL

To meet the conditions noted before an apparatus was used in this investigation which was a modification of that developed by Johnson and Hammer[1] at Iowa State College for the determination of the specific heats of milk and milk products.

Fig. 1 is a diagram of the apparatus. The material to be studied is contained in a 200 cc. Dewar Bulb C, which is in a pasteboard cup A, the space between the Dewar bulb and the outer cup being filled with loosely packed, granulated asbestos. Heat was supplied by means of the manganin heating coil, E, which was sealed in a glass tube filled with oil. The apparatus was also equipped with a copper stirrer, F, and thermometer, D, which could be read to .01 degree by means of a magnifying lens. Current was supplied to the coil from ten volt direct current mains through an ammeter. In those determinations which were carried out at room temperature, the order of procedure at first adopted was as follows: The Dewar bulb in its insulating cup was weighed and a volume of about 200 cubic centimeters of the oil which had been previously cooled to about three degrees below room temperature was introduced into it after which it was weighed again. The stirrer was then operated until the temperature began to rise steadily, when the current was turned on and allowed to flow through the coil for two minutes,

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[1] J. Am. Chem. Soc. 35, 945-48.

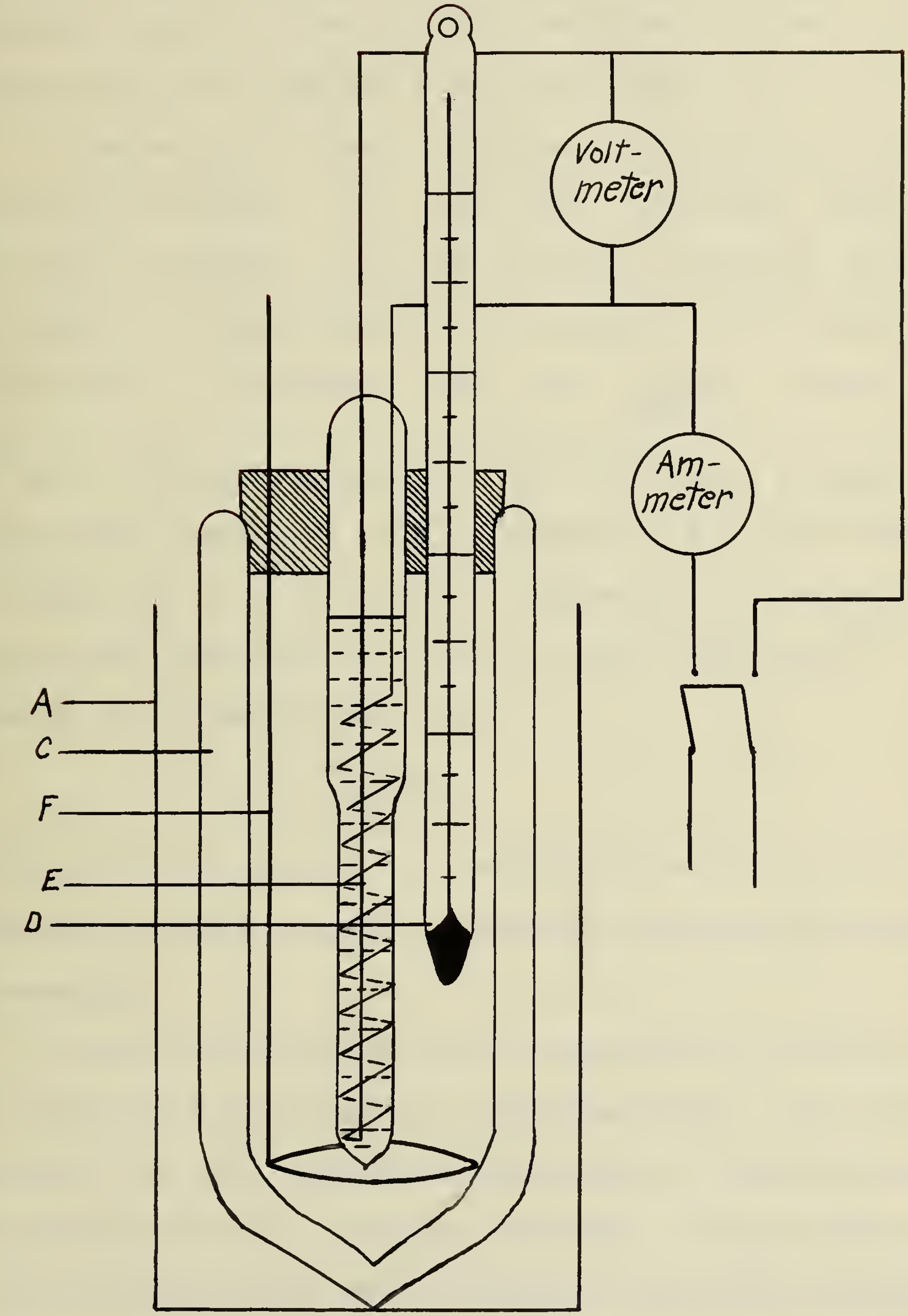
Volt-meter
Am-meter
A
C
F
E
D

Fig. 1.

the ammeter and voltmeter (connected across the coil) being read. The stirrer was then operated continuously until the temperature ceased to rise and fell uniformly. The highest temperature was read and the rise calculated.

The amount of heat liberated in the coil was calculated by the formula $H = .238\ I^2RT = .238\ EIT$, where T is the time in seconds, I is the current in amperes, and E is the reading of the voltmeter. The specific heat was then calculated from the formula $\text{Sp. Heat} = \frac{H - Mt}{wt}$, where H is the heat liberated as obtained from the above formula, M is the water equivalent of the apparatus, w is the weight of oil taken and t is the rise in temperature. The water equivalent was determined by several runs using water in the Dewar bulb, the formula used being

$$M = \frac{H - wt}{t},$$

where H is heat liberated, w is weight of water, t is rise in temperature. The results of several determinations were then averaged.

Using the value for water equivalent thus obtained and the apparatus and procedure described above, runs were made using olive oil, glycerine and toluol. These did not check as well as might have been expected. It was thought that the stirring device was inefficient and that inasmuch as the oil surrounding the heating coil as well as that in the cup was in general a poor conductor, the temperatures

of different parts of the liquid were not quickly equalized and so errors arose through excessive radiation, the thermometer never recording the true maximum temperature.

To overcome this difficulty a new stirrer was devised having more surface. As some difficulty had also been experienced in getting a good reading of voltage, the actual resistance of the coil was determined by means of a Wheatstone bridge and the formula for calculating heat liberated was used in the form

$$H = .238\ I^2RT$$

R being the resistance of the coil in ohms.

To cut down the time during which radiation could take place a new procedure was adopted as follows:

The oil, previously cooled to about three or four degrees below room temperature, was introduced into the Dewar bulb with the coil and stirrer in place, and current was run through the coil for thirty seconds. The stirrer was then operated for three minutes, the temperature of the oil noted and the current again turned on and allowed to run two minutes. Readings of current were taken every fifteen seconds and averaged. The stirrer was operated for five seconds just at the beginning of the last thirty seconds. As soon as the current was shut off the liquid was stirred for three minutes. The temperature read at the end of this period was taken as the highest temperature and the rise calculated from it. In reality the temperature was still rising but it was assumed that the heat still remaining in the coil, which had not af-

fected the thermometer, was offset by that heat remaining, and since the periods of preliminary stirring and final stirring were the same, the difference between the temperature readings at the end of those two periods should give the actual rise due to the heat liberated in the two minutes heating.

Using this procedure the water equivalent was redetermined and more runs were made using olive oil, glycerine and toluol which were found to check very well.

In the determination of the specific heats of the fats and oils studied, three determinations were made with each one, the average being taken. Very good checks were obtained with those oils which were liquid at ordinary temperatures. These were corn oil, rape seed oil, soy bean oil, cocoanut oil, lard oil and red oil. Later sesame oil, cotton seed oil, peanut oil, castor oil and linseed oil were also run. There were also two solid fats; palm oil, melting point 35°-40° and butter fat, melting point 20°-25°. These had to be run at temperatures considerably above room temperature and this necessitated special radiation corrections. As explained under General Discussion, a curve was first plotted showing the rate of loss of heat by radiation at different temperatures. The same procedure was then followed as had been followed with the liquid oils except that readings were taken of temperature at ten second intervals during the three minute stirring period in which the temperature was rising. A curve could then be

plotted showing the temperatures at different times. By adding to each reading the rate of radiation loss as determined from the first curve a new temperature-time curve could be drawn which would show the actual temperatures and the actual rise. By using this sort of correction it was found that the radiation lost introduced considerable error especially in the case of palm oil which had to be studied at somewhat above room temperature.

Table I shows the results of the determinations of the specific heats of the first eight fats and oils received from Morris and Company together with the results of some runs on other oils obtained from various sources. These were all determined at room temperature with the exception of palm oil and butter fact, the former of which was determined at sixty degrees and the latter at thirty-five degrees.

The other constants given for the first eight fats and oils were determined in connection with this study in order to ascertain the quality of the samples. Most of the constants for the other oils were taken from tables given by Lewkowitsch for the particular grade of oil used. The Iodine number was determined by the method of Hanus.

TABLE I

Oil	Sp.Gr.	Sap.val.	Iodine No.	Sp.Heat.
Corn	.923	189	126	.455
Soy Bean	.924	197.3	129	.457
Rape Seed	.915	170.1	102.3	.456
Lard	.916	196.3	73.3	.459
Cocoanut	.926	264.2	7.15	.469
Palm (solid)	.921 (50°)	198.2	52.8	.658
Butter fat (solid)	.918 (25°)	231.4	39.5	.525
Red Oil	.920	197.5	134.7	.465
Olive	.912	190.0	83.	.464
Sesame	.921	189	107.	.458
Peanut	.914	192	91.6	.463
Cotton seed	.925	193	108.	.433
Castor	.960	179	86.2	.588
Linseed (boiled)	.945	190	169.9	.400
Chinese Wood	.941	192	163	.415

After carrying out the above work, it was decided to attempt to ascertain the variation of specific heat with temperature. In doing this, runs were made at a temperature about fifteen or twenty degrees higher than the previous runs had been made. In all of these cases radiation corrections had to be made as above. This was of especial interest in the case of plam oil and butter fat in that it gives an opportunity of determining how the specific heat was affected by the heat of fusion when determined in the neighborhood of the melting point.

Table II shows the results of these determinations.

Oil	Temp.	Sp. Heat	Temp.	Sp. Heat
Corn	20°	.455	35°	.455
Soy Bean	20°	.457	35°	.458
Cotton seed	20°	.433	30°	.432
Cocoanut	20°	.469	30°	.469
Sesame	20°	.458	35°	.460
Butter fat	25°	.525	60°	.485
Palm oil	50°	.658	60°	.624

As shown by the above table, the specific heats of oils well above their melting points do not show any appreciable change of specific heat with change of temperature, such change being at least to small to be detected by the method used.

It appears, however, that with oils which are examined at close to the melting point, the specific heat de-

creases for a short time before the normal increase begins to occur, if it does occur. This is probably due to the fact that these fats, not having a definite melting point, do not take up the heat of fusion all at once but this process is spread out over a comparatively wide range. As we get farther from the melting point, there is less of this heat of fusion which is taken up and apparently, in this region, the specific heat decreases. It is impossible to separate the true specific heat from this heat of fusion, but if it were, it would probably show that the specific heat is fairly constant for small changes of temperature.

V CONCLUSION

In considering the accuracy of the above work, there seems to be no reason for doubting the accuracy of those determinations made at room temperature. The apparatus was well insulated and the procedure so regulated as to allow as little error as possible to come in through radiation losses. In that work done at higher temperatures the accuracy depended mainly upon the radiation correction. In determining the rate of cooling of the apparatus, corn oil was used because the value of its specific heat was very nearly an average. The error introduced by this would be largest in the case of those oils whose specific heats varied appreciably from that of corn oil. Making due allowance for this, however, it seems that these results should be fairly accurate to the third decimal place.

Some of the conclusions which may be drawn from the above work are as follows:

1. In considering methods of determining specific heats, the method using the adiabatic calorimeter, in which the oil is used as a heat absorbing bath and a standard substance is burned, is probably best when samples of the oil are obtainable in quantities of one to two liters. In case much smaller quantities are to be worked with, the method used here was found satisfactory.

2. It was found that the specific heats of most

of the liquid oils studied were within a small range, that is, between .455 and .469. The notable exceptions to this were cotton seed oil, boiled linseed oil and castor oil. That the specific heat of boiled linseed oil should be low might be expected since it contains a certain amount of metallic salts of organic acids in solution. Since inorganic materials in general have much lower specific heats than organic substances, it might be expected that the specific heats of the metallic salts of organic acids might be lower than those of the acids themselves.

For cotton seed oil no explanation of its rather low specific heat can be given unless the sample used had been subjected to some special treatment before being run.

Castor oil, which is a very viscous oil, approached more nearly the high specific heats of the solid fats, as might have been expected.

3. No variation, as a class, could be picked out between drying and non-drying oils when both were examined in the raw condition.

4. No great change of specific heat could be observed with a change of temperature in the case of the liquid oils. Those fats which were solid at room temperature, in whcih case the specific heats were determined just above the melting point, showed a fall in the specific heat with a small increase of temperature, which as noted above was accounted for by the fact that the heat of fusion and specific heat were indistinguishable from each other at these temperatures.

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